

PATENT SPECIFICATION

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(54) PRODUCTION OF MICROSPHERES

(71) We, AGIP NUCLEARE S.P.A., an Italian company, of Piazza E. Mattei, 1, Rome, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for the production of carbon-containing microspheres of an oxide of at least one metal selected from thorium, uranium and plutonium.

The term "microsphere" is used herein to mean a small sphere without any particular limitation as to size.

Microspheres of thorium, uranium or plutonium oxide and of oxides of their mixtures, which contain carbon, are used either as fuel for high temperature gas-cooled nuclear reactors, or in the production of carbide microspheres which in their turn can be used in reactors of this type or of different types.

It is desirable that the carbon is distributed as homogeneously as possible, and that the microspheres have a good compactness and solidity.

Microspheres of thorium, uranium and plutonium oxides, containing carbon, may be obtained by adding finely divided carbon to a starting solution of compounds of thorium, uranium or plutonium, as is described in our Italian Patent Specifications Nos. 727,301 and 778,786. In fact finely divided carbon (carbon black) can be dispersed in a solution of a uranium salt (for example uranyl nitrate), and of thorium and/or plutonium salts, together with a polymer soluble in H₂O, and the resulting solution can be dripped into aqueous ammonia solution to produce microspheres. After an ageing of the resulting microspheres in the aqueous ammonia solution for about 2 hours, the microspheres are subjected to a rapid washing with water to remove the foreign ions, for example, NH₄⁺ and NO₃⁻, and are then dried.

The dried microspheres are subsequently subjected to a thermal treatment at an elevated temperature.

The microspheres thus produced can, depending on the content of carbon, be soft or brittle or have a low abrasion resistance.

According to the present invention, there is provided a process for producing carbon-containing microspheres of one or more metals in oxide form, selected from thorium, uranium and plutonium, which process comprises forming a mixture of: (i) a solution of one or more compounds of the one or more metals and (ii) an organic substance which is polymerizable in an alkaline medium and which is totally monomeric or only partially polymerized; forming microspheres from the resulting mixture in an alkaline medium and causing polymerization of the organic substance in the same or different alkaline medium; and heating the microspheres to a degree sufficient, and in an atmosphere appropriate, to cause carbonization of the polymerized organic substance in the microspheres. Preferably at least part of the heating of the microspheres is effected in an atmosphere of argon and carbon monoxide.

In the process of the present invention, the polymerizable or partially polymerized organic substance frees the required carbon during the thermal treatment subsequent to the formation of the microspheres.

In the process of the present invention, the starting solution, i.e. the solution to be used in the formation of the microspheres, is prepared by mixing with a solution of a thorium, uranium and/or plutonium salt, a polymerizable and/or partially pre-polymerized organic substance polymerizable in an alkaline ambient; an example of the organic substance is acrolein, acrylonitrile, or a solution of styrene in benzene. Such organic substances may be used in a mixture of two or more, or with co-polymerizing substances or graft polymers. If in the starting solution there is also present a pre-polymerized and/or partly polymerized substance, this can be one obtained by thermal polymerization and/or in an acidic or alkaline ambient. If the organic substance is acrolein or acrylonitrile and is not miscible with or soluble in the

aqueous solution of the thorium, uranium and/or plutonium salt(s), there may be added a solvent to promote mixing, for example tetrahydrofurfuryl alcohol or isopropyl alcohol.

Once prepared, the starting solution can be converted into spheroidal particles by making use of one of the techniques known in the art, involving an alkaline medium. The spheroidal particles may be collected in the alkaline solution and left for a time sufficient to complete the precipitation of the hydroxides and/or of the insoluble salts of thorium, uranium and/or plutonium and to ensure a sufficient degree of polymerization of the organic substance added to the starting solution. An example of a suitable time is 2 hours. Alternatively, when the content of thorium, uranium and/or plutonium is very low, the microspheres obtained from the starting solution may be collected in a tower through which is passed in countercurrent to the microspheres, a heating gas comprising ammonia alone or ammonia in admixture with an inert gas (e.g. nitrogen) or air.

After the formation of the microspheres, by precipitation of the hydroxides and/or of the thorium, uranium and plutonium salts, the microspheres are generally subjected to washing with H_2O to remove foreign ions. The microspheres can then be dried, for example, by an air current heated by means of electrical resistances, by an infra-red lamp, or by microwaves at high frequency. These heating methods affect the properties of the final product, particularly the density and the tensile strength of the microspheres. Another method of drying which may be used is based on an azeotropic distillation according to which the washed particles are dispersed in an organic liquid immiscible with water and are kept boiling for a sufficient time to effect drying. The properties of the final product depend, in this case, on the organic liquid used and particularly on its boiling temperature.

The dried particles are subjected to thermal treatments which may differ depending on the composition and on the properties required for the final product.

The process of the present invention makes it possible to obtain microspheres of the desired oxide, containing carbon in a quantity which may vary from a practically negligible value (a few parts per million) to a considerable quantity.

When operated under optimum conditions, the process of the present invention makes it possible to produce microspheres possessing exceptional characteristics of sphericity, high tensile strength, uniform dispersion of the carbon in the microspheres, and high density.

The accompanying drawing represents three beakers 1, 2 and 3 and is referred to in the

following Examples which illustrate the present invention.

In certain Tables appearing in the Examples there appears the abbreviation "C/U" which represents the number of carbon atoms per uranium atom in the product. Similar remarks apply to "C/Th".

EXAMPLE 1

100 cc of 8% (by weight) aqueous ammonia were poured into a beaker 1 (see Figure 1) and were kept stirred.

A mixture of 100 cc of acrolein and 100 cc of furfuryl alcohol, prepared in beaker 2 was added slowly to the contents of beaker 1. The addition of the mixture was effected sufficiently slowly to keep the temperature below $90^{\circ}C$, because of the exothermic reaction which developed. The stirring was continued until the temperature of the resulting polymeric liquid had reached about $60^{\circ}C$. At this point beaker 1 and its contents were cooled with the aid of a bath of cold water. There was then added with stirring at room temperature to the contents of the beaker 1 a mixture of 200 cc of uranyl nitrate solution (565 g/litre, as UO_2), 360 cc of tetrahydrofurfuryl alcohol, 70 cc of water and 150 cc of Methocel 90 H G (3% by weight) previously prepared in beaker 3. The word "Methocel" is a Registered Trade Mark, and Methocel 90 HG is a methyl isopropyl cellulose.

The resulting solution was then used in the production of microspheres using a suitable dripping device in 32% (by weight) aqueous ammonia. The resulting microspheres were aged in 32% (by weight) aqueous ammonia, for 2 hours. During this time the reaction of the uranyl nitrate with ammonia was completed to give the insoluble precipitate of ammonium diuranate, and there continued the polymerization of the monomer contained in the microspheres.

After ageing, the microspheres were washed with water to remove the foreign ions and subjected to drying by means of an azeotropic distillation with an organic liquid selected from 1,1,1 - trichloroethane, carbon tetrachloride and xylene.

After drying, the microspheres were subjected to the following thermal treatment: they were heated at a rate of 200 Centigrade degrees per hour up to $600^{\circ}C$ in an atmosphere of argon plus 4% by volume of hydrogen, then at a rate of 350 Centigrade degrees per hour up to $1300^{\circ}C$ in an atmosphere of argon plus 4% by volume of CO , and then the temperature was kept constant at $1300^{\circ}C$ for 2 hours. The microspheres were then cooled to room temperatures using a procedure reversed to that used for the heating: thus, starting from $1300^{\circ}C$ in an atmosphere of argon and CO , the temperature was brought to $600^{\circ}C$ by cooling at 350° per hour and

then in an atmosphere of argon and hydrogen the cooling was continued to room temperature at a rate of 200° per hour.

The characteristics of the microspheres were:

	Drying in 1,1,1-trichloroethane	Drying in carbon tetrachloride	Drying in xylene
C/U	4.9:1	4.9:1	4.9:1
Density (g/cc)	2.9	3.1	2.7
mean tensile strength (kg)	3.0	3.0	2.7

EXAMPLE 2

200 cc of 8% by weight aqueous ammonia were poured into a beaker 1 and kept stirred. A mixture of 200 cc of acrolein and 200 cc of furfuryl alcohol, prepared in beaker 2, was added slowly to beaker 1. The addition of the mixture was carried out sufficiently slowly to ensure that the temperature did not rise above 90°C, because of the exothermic reaction which developed. The stirring was continued until the temperature of the resulting polymeric liquid decreased to about 60°C.

The beaker 1 and its contents were cooled with the aid of a bath of cold water. There was then added with stirring at room temperature to the contents of beaker 1, a mixture of 200 cc of uranyl nitrate solution (565 g/l, as UO_2), 200 cc of tetrahydrofurfuryl alcohol, 50 cc of water and of 100 cc of Methocel 90 HG 3% by weight, prepared in beaker 3.

The resulting solution was then used in the production of microspheres, using a suitable dripping device in 32% by weight aqueous ammonia. The microspheres were aged for 2 hours in 32% by weight aqueous ammonia and subsequently washed with water. The microspheres were dried by azeotropic distillation with an organic liquid selected from 1,1,1-trichloroethane, carbon tetrachloride and xylene.

After drying, the microspheres were subjected to the following thermal treatment: 200° per hour up to 600°C in an atmosphere of argon plus 4% by volume of hydrogen; 350° per hour up to 1300°C in an atmosphere of argon plus 4% by volume of carbon monoxide; the temperature was kept constant for two hours at 1300°C. Then the microspheres were cooled to room temperature in a reverse procedure to that used in the heating. The characteristics of the microspheres were:

	Drying in 1,1,1-trichloroethane	Drying in carbon tetrachloride	Drying in xylene
C/U	9.6:1	9.6:1	9.6:1
Density (g/cc)	2.35	2.45	3.1
tensile strength (kg)	2.2	3.3	4.0

EXAMPLE 3

200 cc of an 8% by weight aqueous ammonia solution were poured into beaker 1 and were kept stirred. To the contents of beaker 1 were added slowly a mixture of 200 cc of acrolein and 200 cc of furfuryl alcohol, prepared in a beaker 2. The mixture was poured slowly from beaker 2 into beaker 1 as described in Examples 1 and 2. When the temperature of the resulting polymeric liquid decreased to about 60°C, the beaker 1 was cooled with the aid of a bath of cold water.

At room temperature, a mixture of 200 cc of uranyl nitrate solution (565 g/l, as UO_2), 250 cc of tetrahydrofurfuryl alcohol and 100 cc of water, prepared in beaker 3, was poured into beaker 1, with stirring. The resulting solution was left at a temperature not higher than 18–20°C for about 10 hours. The monomer contained in the solution continued to polymerize slowly.

After 10 hours, the viscosity of the solution was such that it could be formed into

microspheres by means of a dripping device. The mixture was dripped into a 32% by weight aqueous ammonia solution.

The microspheres were aged for 2 hours in a 32% by weight aqueous ammonia solution and subsequently washed in water. The microspheres were then dried in a furnace at 100°C by means of heating with electric resistances or with high frequency microwaves. The microspheres had now become dark red. Subsequently the microspheres were subjected to the following thermal treatment: 120° per hour up to 600°C in an atmosphere of argon plus 4% by volume of hydrogen; then the temperature was kept at 600°C for 1 hour; 350° per hour up to 1500°C in an atmosphere of argon plus 4% by volume of carbon monoxide; and afterwards the temperature was kept constant at 1500°C for 1 hour. Thereafter the microspheres were cooled following a reverse procedure to that employed during the heating.

The characteristics of the microspheres were as follows:

	Drying in electric furnace	Drying with microwaves
C/U	9.8:1	9.8:1
density (g/cc)	3.6	3.7
tensile strength (kg)	6.0	2.0

EXAMPLE 4

100 cc of an 8% by weight aqueous ammonia solution were poured into beaker 1 and were kept stirred.

A mixture of 100 cc of acrolein and 100 cc of furfuryl alcohol, prepared in beaker 2, was added slowly to beaker 1, as described in Examples 1 and 2. When the temperature of the resulting polymeric liquid decreased to about 60°C, beaker 1 was cooled with the aid of a bath of cold water.

At room temperature there was added to beaker 1 with stirring, a mixture of 200 cc uranyl nitrate solution (565 g/l, as UO_2), 375 cc of tetrahydrofurfuryl alcohol and 200 cc of water, previously prepared in beaker 3. The resulting solution in beaker 1 was left at a temperature not higher than 18–20°C for 15 hours. The monomer contained in the solution continues to polymerize slowly. After 15 hours, the viscosity of the solution was such that it could be formed into microspheres by making use of a dripping device. The solution was dripped into a 32% by weight aqueous ammonia solution. The microspheres produced in this manner were aged for 2 hours in 32% by weight of aqueous ammonia solution and subsequently washed with water. The microspheres were dried in a furnace heated to 100°C by electrical resistances.

Subsequently the microspheres were subjected to the following thermal treatment: heating at a rate of 120° per hour to 600°C in an atmosphere of argon plus 4% by volume of hydrogen, keeping at 600°C for an hour, further heating at a rate of 350° per hour to 1500°C in an atmosphere of argon plus 4% by volume of carbon monoxide, and keeping at 1500°C for an hour. The microspheres were cooled in a reverse procedure to that adopted for heating.

The characteristics of the resulting microspheres were as follows:

	Drying in electrical furnace
C/U	4.8:1
density (g/cc)	4.1
tensile strength (kg)	2.0

EXAMPLE 5

200 cc of an 8% by weight aqueous ammonia solution were poured into a beaker 1 and kept stirred. A mixture of 200 cc of acrolein and 200 cc of furfuryl alcohol was added to beaker 1, the alcohol having been previously prepared in beaker 2. The addition of the

mixture was carried out sufficiently slowly to prevent the temperature from exceeding 90°C, because of the exothermic reaction which develops. The stirring was continued until the temperature of the resulting polymeric liquid decreased to about 60°C. Beaker 1 was cooled with a bath of cold water. At room temperature, a mixture of 200 cc of thorium nitrate (330 g/l, as ThO_2), 200 cc of tetrahydrofurfuryl alcohol, 50 cc of water and 100 cc of Methocel 90 HG (3% by weight), previously prepared in beaker 3, was poured into beaker 1 at room temperature. The resulting solution was allowed to age for 1 hour, and then it was dripped into a 32% by weight aqueous ammonia solution. The resulting microspheres were allowed to age for two hours in a 32% by weight aqueous ammonia solution and subsequently were washed with water. They were then dried by means of azeotropic distillation with carbon tetrachloride.

After drying, the microspheres were subjected to the following thermal treatment: heating at a rate of 200° per hour to 600°C in an atmosphere of argon plus 4% by volume of hydrogen, heating at a rate of 350° per hour up to 1300°C in an atmosphere of argon plus 4% by volume of carbon monoxide, and keeping at the temperature of 1300°C for two hours. The microspheres were then cooled to room temperature in a procedure the reverse of that used for the heating.

The characteristics of the microspheres are:

	Drying with carbon tetrachloride
C/Th	18.5:1
density (g/cc)	1.53
tensile strength (kg)	1.1

WHAT WE CLAIM IS:—

1. A process for producing carbon-containing microspheres of one or more metals in oxide form, selected from thorium, uranium and plutonium, which process comprises: forming a mixture of (i) a solution of one or more compounds of the one or more metals and (ii) an organic substance which is polymerizable in an alkaline medium and which is totally monomeric or only partially polymerized; forming microspheres from the resulting mixture in an alkaline medium and causing polymerization of the organic substance in the same or a different alkaline medium; and heating the microspheres to a degree sufficient, and in an atmosphere appropriate, to cause carbonization of the polymerized organic substance in the microspheres.

2. A process according to Claim 1, wherein at least part of the heating of the microspheres is effected in an atmosphere of argon and carbon monoxide.

3. A process according to Claim 1 or 2, wherein the polymerizable organic substance is acrolein, acrylonitrile or styrene.

5 4. A process according to Claim 3, wherein, when the organic substance is acrolein or acrylonitrile, there is present a solvent selected from tetrahydrofurfuryl alcohol and isopropyl alcohol.

10 5. A process according to Claim 3, wherein, when the organic substance is styrene, there is present benzene as solvent.

15 6. A process according to any preceding Claim, wherein the mixture additionally includes a copolymerizable substance or a graft polymer.

20 7. A process according to any preceding Claim, wherein the organic substance, when partially polymerized, is one partially polymerized by thermal polymerization and/or in an acidic medium.

8. A process according to Claim 1, substantially as described in any one of the foregoing Examples 1 to 5.

9. Microspheres whenever produced by a process according to any preceding Claim. 25

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COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of
the Original on a reduced scale*

